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PATENT SPECIFICATION

NO DRAWINGS

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140, P3(B:F2:F7:G4:G5).

International Classification:—C07c. D06m.

COMPLETE SPECIFICATION

Improvements relating to Insecticidal Compounds and their use

DIV

We, J. R. GEIGY A.—G., a body corporate  
organised according to the laws of Switzerland,  
of 215 Schwarzwaldallee, Basle,  
Switzerland, do hereby declare the invention,  
for which we pray that a patent may be  
granted to us, and the method by which it is to  
be performed, to be particularly described  
in and by the following statement:—

The present invention concerns insecticidal  
agents, processes for the production thereof  
and their use for the protection of keratine  
material against destruction caused by injurious  
insects. The invention also concerns, as  
industrial product, the material protected  
by these agents from destruction caused by  
injurious insects.

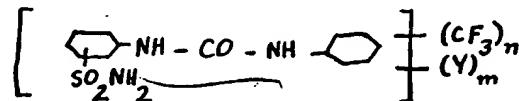
Various processes concerning the production  
of sulphonated insecticidal agents are already  
known. However, compounds with sulphonic  
acid groups only draw completely onto keratine  
material, for example, wool, from a relatively  
strongly acid bath. Insecticidal agents are often applied in the dyebath when dyeing  
the wool. When dyestuffs needing only a slight  
amount of acid or having slight migratory  
power are used, such as for example complex  
heavy metal compounds of monoazo dyestuffs  
having no acid dissociating groups, the  
presence of acid in the dyebath has an adverse  
effect on the evenness of the wool dyeing.  
There is, therefore, a need for insecticidal  
agents which draw onto wool from a neutral  
to weakly acid dyebath and can, therefore, be  
applied with complex heavy metal compounds  
of unsulphonated azo dyestuffs. Thus, protective  
agents against injurious insects which have  
sufficient drawing power from a neutral bath  
are a valuable contribution to the art.

In this connection, the treatment of keratine  
material with insecticidal agents which have  
no sulphonic acid groups and are insoluble in  
water has already been suggested. This was  
done by using aqueous emulsions of such  
agents in the preparation of the dyebaths.  
However, it is difficult to make such emulsions.

[Price 3s. 6d.]

sions durable and often undesirable precipitates occur in the dyebath.

It has now been found that water soluble  
compounds having no sulphonic acid groups,  
which compounds have good activity against  
insects that are injurious to keratine fibres,  
are obtained if an isocyanate of the aromatic  
series is reacted with an aromatic amine, the  
components being so chosen that an  $H_2N - SO_2 -$  group is introduced with the aromatic  
amine and at least two substituents selected  
from aromatically bound halogen atoms or  
trifluoromethyl groups are present in the reaction  
product, which corresponds with the formula:



wherein Y represents a halogen atom  
n represents an integer from 0 — 2 and  
m represents an integer from 0 — 5  
and wherein n + m are at least 2.

For technical and economical reasons, chiefly  
chlorine is meant by halogen atoms, however,  
the corresponding derivatives substituted by  
bromine, fluorine and iodine can also be used.

The insecticidal compounds produced  
according to the present invention are new.  
Their production by reacting isocyanates of  
the aromatic series with the aromatic amino  
compounds occurs under conditions which are  
usual for such reactions which are known per  
se.

4 - Chlorophenyl isocyanate, 3,4 - dichlorophenyl isocyanate, 3,4,5 - trichlorophenyl isocyanate, 3 - trifluoro - methylphenyl isocyanate, 3 - trifluoromethyl - 4 - chlorophenyl isocyanate and 3 - chloro - 4 - trifluoromethylphenyl isocyanate can be used as aromatic isocyanates.

Examples of aromatic amines which can be

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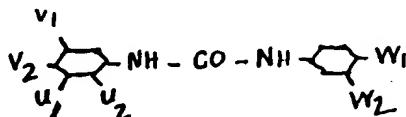
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used are 2- or 3- or 4-amin benzene sulphonic acid amide, 3-amino-4-chloro or 2-chloro-5-aminobenzene sulphonic acid amide, 2,3-dichloro-5-amino- or 2-amino-4,5-dichlorobenzene sulphonic acid amide, and in addition 2-trifluoromethyl-4-aminobenzene sulphonic acid amide and 2-amino-4-trifluoromethyl-5-chlorobenzene sulphonic acid amide.

As valuable compounds which can be used according to the present invention chiefly those can be named in which at least one aromatic radical is substituted in two positions by halogen atoms and/or trifluoromethyl groups, this substitution advantageously being by halogen and trifluoro methyl substituents in the *p*- and *m*-positions to the urea bridging member. Particularly active are those derivatives in which the  $\text{H}_2\text{N}-\text{SO}_2-$  group is in the *m*- or preferably in the *o*-position to the  $-\text{NH}-\text{CO}-\text{NH}$  group.

Thus the most valuable compounds correspond with the general formula:



wherein one U represents  $-\text{SO}_2\text{NH}_2$ ,  
25 the other U represents hydrogen  
one V represents chlorine or the trifluoromethyl group,  
the other V represents hydrogen or chlorine  
one W represents chlorine or the trifluoromethyl group, and  
the other W represents chlorine.

The activity of such compounds containing the  $\text{H}_2\text{N}-\text{SO}_2-$  group could not have been foreseen, as if known sulphonated insecticidal agents are converted into the corresponding  $\text{H}_2\text{N}-\text{SO}_2-$  derivatives by modification of their sulphonic acid group the insecticidal action is reduced to a great extent. Thus for example, 2,2<sup>1</sup>-dihydroxy-3,3<sup>1</sup>,5,5<sup>1</sup>-4<sup>11</sup>-40 pentachloro-triphenyl methane - 2<sup>11</sup>-sulphonic acid amide has not sufficient insecticidal activity for practical purposes when compared with the corresponding sulphonic acid.

45 The new compounds according to the present invention, however, have remarkable insecticidal activity and can be used in particular for the protection of keratine material against injurious pests such as the larvae of moths, 50 fur and carpet beetles. In the form of their alkali metal salts, e.g. the lithium, sodium and potassium salts, they have sufficient water solubility to be applied to keratine material from such solutions. When applied during the 55 dyeing process the compounds draw onto keratine material, e.g. wool, completely from a neutral to weakly acid bath and they are fast to washing and rubbing. As has already been explained, such insecticidal agents are very

advantageous as they can be used in the same dyebath with dyestuffs which draw from a neutral to weakly acid medium. However, the new compounds can not only be applied in aqueous solutions. Those which are soluble in organic solvents can also be used in this form for the impregnation of keratine material. Finally, the compounds can also be used in the form of dispersions or in powder form, possibly with carriers, as insecticidal agents.

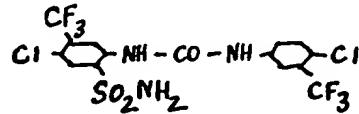
The following examples serve to illustrate the invention. Where not otherwise stated, the temperatures are in degrees Centigrade and the parts are given as parts by weight. The relationship of parts by volume to parts by weight is as that of litres to kilogrammes.

#### EXAMPLE 1

27.4 Parts of 2 - amino - 4 - trifluoromethyl - 5 - chlorobenzene sulphonic acid amide are dissolved at 50-55° in 250 parts of abs. butanone. A solution of 22.1 parts of 3 - trifluoromethyl - 4 - chlorophenyl isocyanate in 220 parts of abs. nitrobenzene is added and the mixture is heated for 16 hours at 40-45° while stirring.

The butanone is then distilled off and, after cooling, 200 parts of chlorobenzene are added to the residue. The precipitate which forms is filtered off, washed with chlorobenzene and dried in a vacuum at 100°.

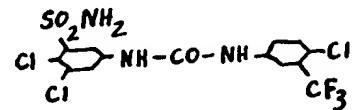
After crystallisation from alcohol, the compound melts at 208-210°. It corresponds to the formula:



Nitrogen determination: found 8.3% N  
calculated 8.4% N

#### EXAMPLE 2

24.1 Parts of 2,3 - dichloro - 5 - aminobenzene sulphonic acid amide and 22.1 parts of 3 - trifluoromethyl - 4 - chlorophenyl isocyanate are reacted as described in Example 1. A white body which melts at 235-237° is obtained. It corresponds to the formula:



Analysis: found 9.0% N  
calculated 8.9% N

#### EXAMPLE 3

24.1 Parts of 2,3 - dichloro - 5 - aminobenzene sulphonic acid amide and 18.8 parts of 3,4 - dichlorophenyl isocyanate are reacted

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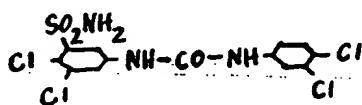
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as described in the process of Example 1. The compound obtained melts at 239-240° and corresponds to the formula:



5 Analysis: found 9.8% N  
calculated 9.8% N

## EXAMPLE 4

0.2 Parts of the compound according to Example 2 are dissolved with dilute caustic soda lye and the solution is brought up to 1000 parts by volume with water. 20 Parts of wool are treated in this solution for 30 minutes at 50°.

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After rinsing, wringing out and drying, the wool is resistant to attack by the larvae of *Tineola bis.*, *Anthrenus vorax* and *Attagenus piceus*.

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The following compounds can be produced in a manner analogous to those described in the above examples:

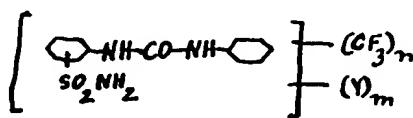
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No.	M. P.
1	251-252°
2	217-219°
3	260-262°
4	253-255°
5	276-278°
6	280-283°
7	282-285°
8	258-262°
9	218-220°
10	243-245°

No.		M. P.
11		233-235°
12		240-242°
13		224-226°
14		226-228°
15		231-233°
16		238°
17		214°
18		259°
19		239°
20		227°
21		183°
22		210-211°
23		193-195°

## WHAT WE CLAIM IS:—

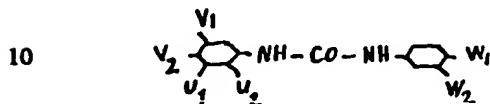
1. A compound having the formula:



5 wherein

Y represents halogen,  
 n represents an integer from 0 — 2,  
 m represents an integer from 0 — 5  
 and wherein n + m are at least 2.

2. A compound having the formula:



10 wherein one U represents  $-\text{SO}_2\text{NH}_2$ ,  
 the other U represents hydrogen,  
 one V represents chlorine or the trifluoro-  
 methyl group,  
 15 the other V represents hydrogen or chlorine  
 and  
 one W represents chlorine or the trifluoro-  
 methyl group and  
 the other W represents chlorine

15 20 3. Process for the production of water  
 soluble insecticidal compounds characterised  
 by reacting an isocyanate of the aromatic  
 series with an aromatic amine, the components  
 being so chosen that an  $\text{H}_2\text{N}-\text{SO}_2$  group and

at least two substituents selected from aromati-  
 cally bound halogen atoms or trifluoromethyl  
 groups are present in the reaction product, the  
 $\text{H}_2\text{N}-\text{SO}_2$  group being introduced with the  
 aromatic amine.

25 4. Manufacture of compounds substantially  
 as described with reference to any of the fore-  
 going examples 1 to 3.

30 5 Compounds whenever prepared or pro-  
 duced by the processes of manufacture parti-  
 cularly described.

35 6. A compound as specified in any of the  
 foregoing examples 1 to 3 or in the Table.

40 7. Process for the protection of material  
 containing keratin fibres characterised by the  
 use of any of the compounds as hereinbefore  
 claimed by a process substantially as described  
 in example 4.

45 8. Materials containing keratin fibres pro-  
 tectively treated with any of the compounds  
 defined in claim 1.

9. Manufacture of agents containing insec-  
 ticidal compounds for treating keratin fibres  
 in an aqueous medium substantially as herein-  
 before described.

50 10. Agents containing insecticidal com-  
 pounds for treating keratin fibres in an  
 aqueous medium whenever produced as  
 claimed in claim 9.

For the Applicants,  
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Reference has been directed, in pursuance  
 of Section 8 of the Patents Act, 1949, to  
 Specification No. 753,171.